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MEMORANDUM FOR PRS (In-House Publication)

06 May 2003

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SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-122**
Greg Drake (AFRL/PRSP) et al., "Structural Effects on the Physical Properties of Ionic Liquids"

5355

(Statement A)

2003 AFOSR Molec Dynamics & Theo Chem Contr Mtg
(San Diego, CA, no date provided) (Deadline: 19 May 2003)

Structural Effects on the Physical Properties of Ionic Liquids

Greg Drake and Tom Hawkins
AFRL/PRSP
Air Force Research Laboratory
Edwards AFB, CA 93524

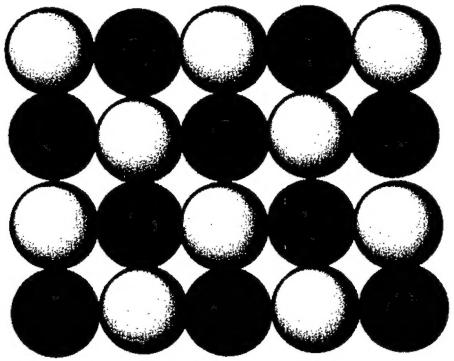
and

John Wilkes
Department of Chemistry
United States Air Force Academy
USAF Academy, CO 80840

Ionic Liquids

NOT

versus



Extended lattice

Table salt Na^+Cl^- m.p. = 804 °C Very high

Cryolite Na_3AlF_6 m.p. nearly 1000 °C (Hall Process for Al production)

Eutectic of Li^+Cl^- and K^+Cl^- m.p. 355 °C

<u>Molten salts are very hot</u>!

Not commercially viable

Corrosion and energy issues

Giant lattice of miniature magnets stuck together

Ionic Liquids

What are Ionic Liquids?
A class of salts consisting of cation/anion pair that has a very low melting point.

Definition of an ionic liquid is open to some debate amongst researchers in the area, but most in the area use one of two.

(1) An ionic compound that melts below 100 °C (b.p. of H_2O). J. Wilkes, P. Wasserscheid, K. Seddon.

(2) An ionic compound that has a melting point at or below ambient temperatures. These are often called RTILs (Room Temperature Ionic Liquids) T. Welton, R. Rogers.

But many of the salts fit both definitions and 2 is really a more specific class of (1).

Ionic Liquids

Important factors affecting the physical properties of ionic liquids

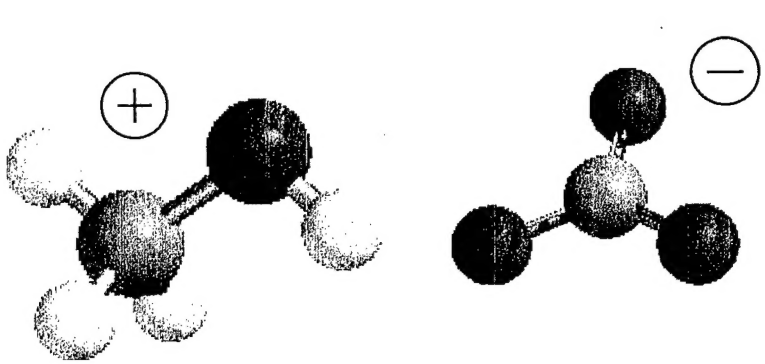
1. Asymmetry of cation as well as anion

2. Packing efficiency

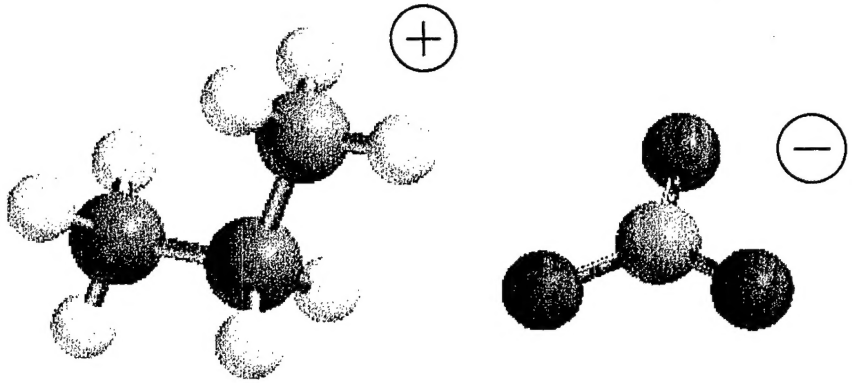
3. Charge delocalization in cationic/anionic species

4. "Sheer size" differentials

Ionic Liquids



Hydroxylammonium nitrate (HAN)
$[NH_3OH^+][NO_3^-]$m.p. 39-40 °C

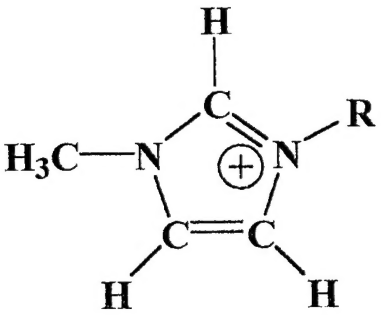


Ethylammonium nitrate
$[CH_3CH_2NH_3^+][NO_3^-]$ m.p. 12 °C

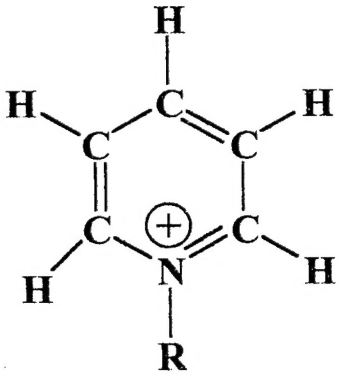
Serious issues...
- can be treacherous
- acidic
-very hygroscropic

Ionic Liquids

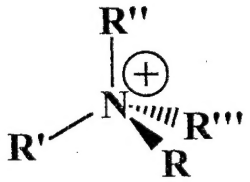
Some major shapes for organic based cations



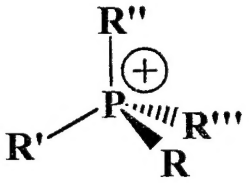
1-methyl-3-alkyl-imidazolium



1-alkylpyridinium



Tetralkylammonium



Tetralkylphosphonium

Ionic Liquids

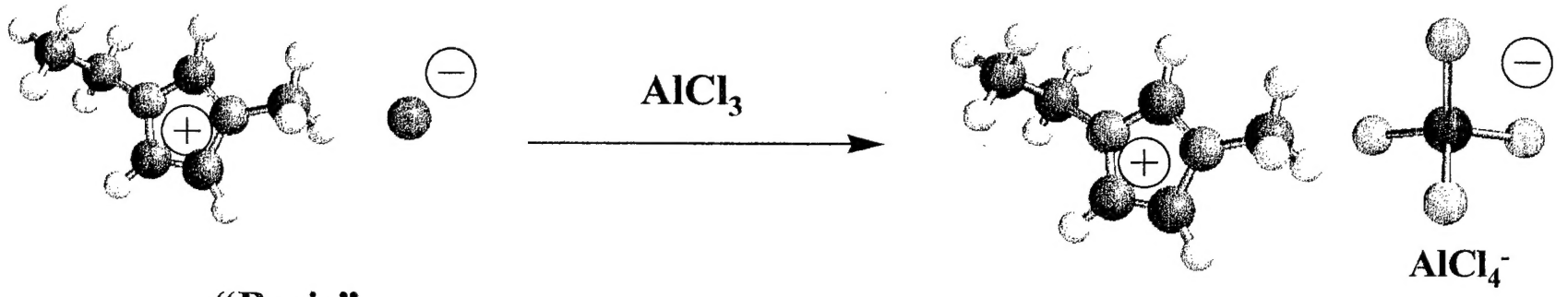
The group of anions for ionic liquids is much larger and growing….

water soluble	water insoluble
$CH_3CO_2^-$	PF_6^-
$CF_3CO_2^-$	$[BR_1R_2R_3R_4]^-$
Cl-, Br-, I-	$[(CF_3SO_2)_2N]^-$
NO_3^-	BF_4^-
BF_4^-	$R\text{-}SO_3^-$
NO_2^-	
$[AlCl_4^-, Al_2Cl_7^-]$	

Typically R groups are n-alkyl groups
This list is not comprehensive but it covers the majority of what is out there.

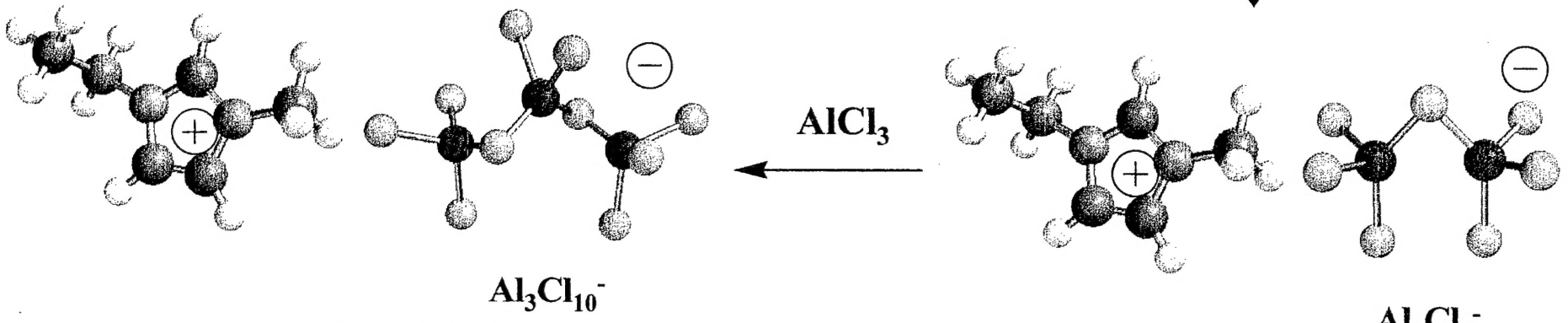
Ionic Liquids

Significant efforts spent on 1-ethyl-3-methyl-imidazolium based systems and aluminum trichloride systems. More complex than originally thought as $AlCl_3$ and Cl^- have an equilibrium based on their respective concentrations.



"Basic"

"Neutral"

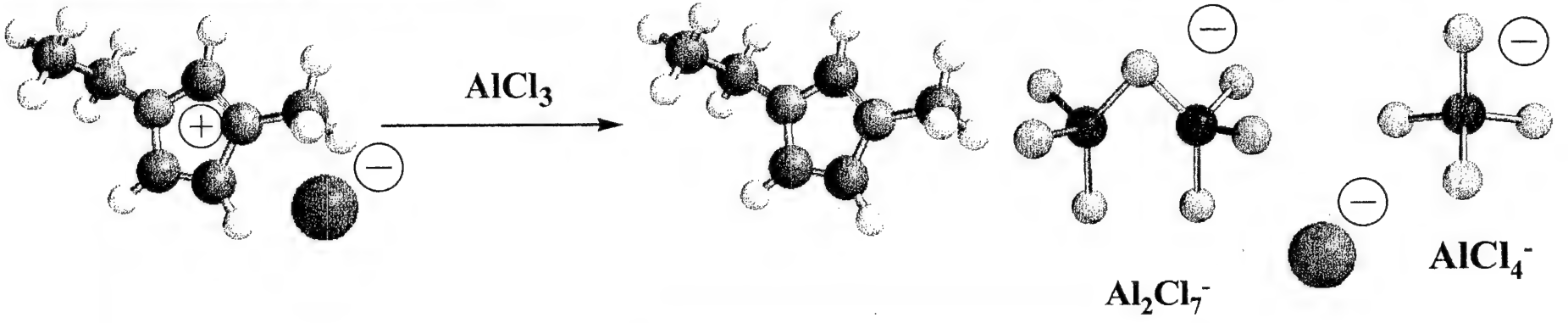


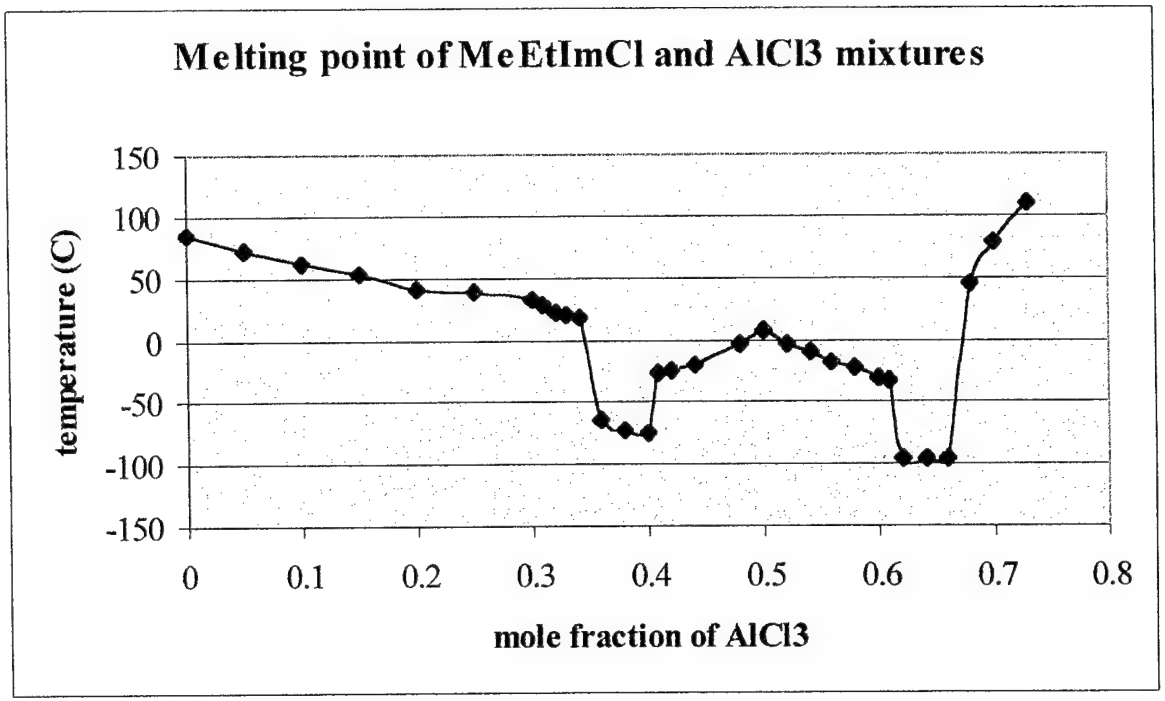
"Strongly acidic"

"Acidic"

Wilkes, J. S. Green Chemistry **2002**, *4*, 3.

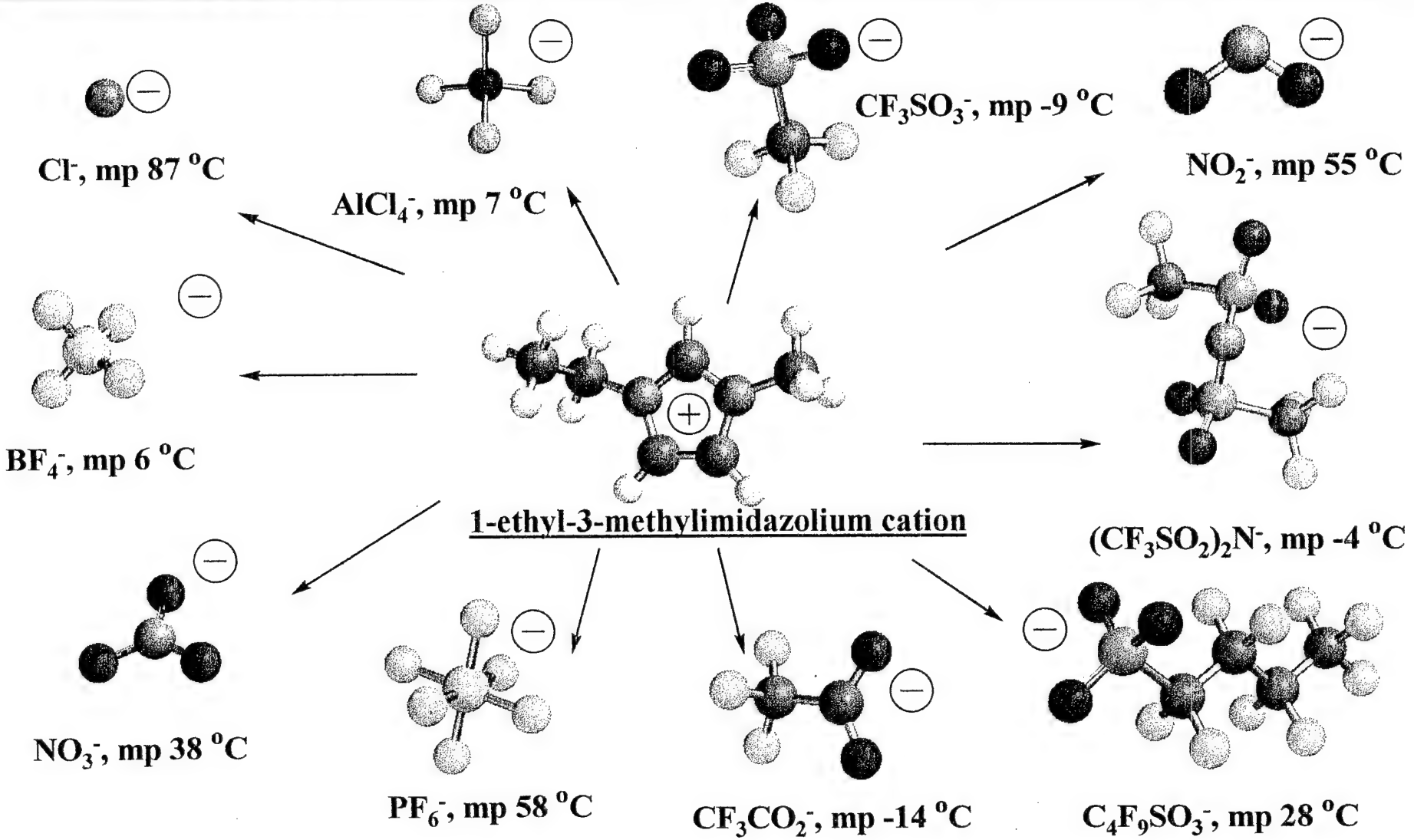
Ionic Liquids





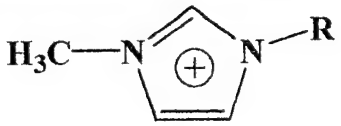
Fannin, A. ; Floreani, D. ; King, L. ; Landers, J. ; Piersma, B. ; Stetch, D. ; Vaughn, R. ; Wilkes, J. ; Williams, J. J. Phys. Chem. **1984**, 88, 2614.

Ionic Liquids



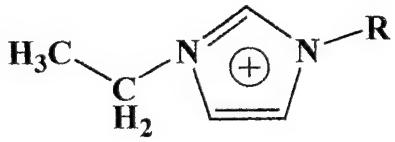
Wasserscheid, P.; Keim, W. Angew. Chem. Int. Ed. Engl. **2000**, 39, 3772. Wasserscheid, P, Welton, T. (eds.) Ionic Liquids in Synthesis Wiley-VCH, FRG, **2003**
.Seddon, K.R. ; Holbrey, J. D. Clean Products and Processes **1999**, 1, 223. Rogers, R.; Seddon, K. (eds.) Ionic Liquids A.C.S. Symp. Ser. 818 2002 A.C.S Publ. Co.

Ionic Liquids melting points



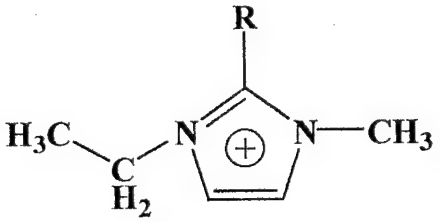
3-methyl-1-R-imidazolium

Substituent	Triflate (m.p.)	Bis(trifluorosulfonamide) m.p.
1-methyl	39	22
1-ethyl	-9	-3
1-butyl	16	-4
1-$CH_2OCH_2CH_3$	27	<-30(Tg)
1-CH_2-CF_3	45	<-30(Tg)



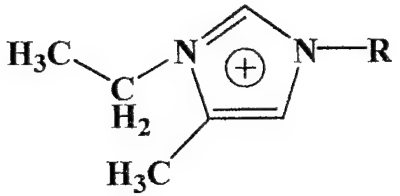
3-ethyl-1-R-imidazolium

Substituent	Triflate (m.p.)	Bis(trifluorosulfonamide) m.p.
1-ethyl	23	14
1-butyl	2	<-30(Tg)



1-ethyl-2-R-3-methyl-imidazolium

Substituent	Triflate (m.p.)	Bis(trifluorosulfonamide) m.p.
2,3-dimethyl	109	20
2-ethyl-3-methyl	113	28

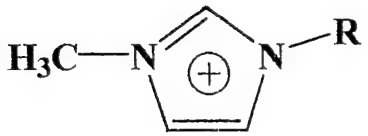


1-ethyl-3-R-5-methyl-imidazolium

Substituent	Triflate (m.p.)	Bis(trifluorosulfonamide) m.p.
3-methyl	6	-3
3-ethyl	35	-22

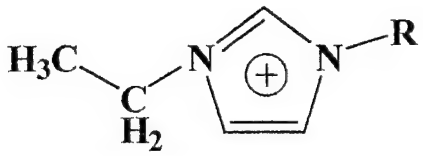
Bonhote, P. ; Diaz, A. ; Papageorgiou, N. ; Kalyanasundaram, K. ; Gratzel, M. Inorg. Chem. **1996**, *35*, 1168.

Ionic Liquids



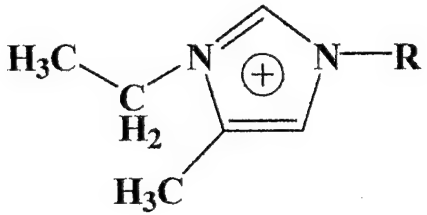
3-methyl-1-R-imidazolium

Bis(trifluoromethylsulfonamide)	η(cP)	Λ(mS/cm)
1-methyl	44	8.4
1-ethyl	34 (45)	8.8 (8.6)
1-butyl	52 (90)	3.9 (3.7)
1-$CH_2OCH_2CH_3$	54 (74)	4.2 (3.6)
1-CH_2-CF_3	248	0.98



3-ethyl-1-R-imidazolium

Bis(trifluoromethylsulfonamide)	η(cP)	Λ(mS/cm)
1-ethyl	35 (53)	8.5 (7.5)
1-butyl	48	4.1



1-ethyl-3-R-5-methyl-imidazolium

Bis(trifluoromethylsulfonamide)	η(cP)	Λ(mS/cm)
3-methyl	37 (51)	6.6 (6.4)
3-ethyl	36	6.2

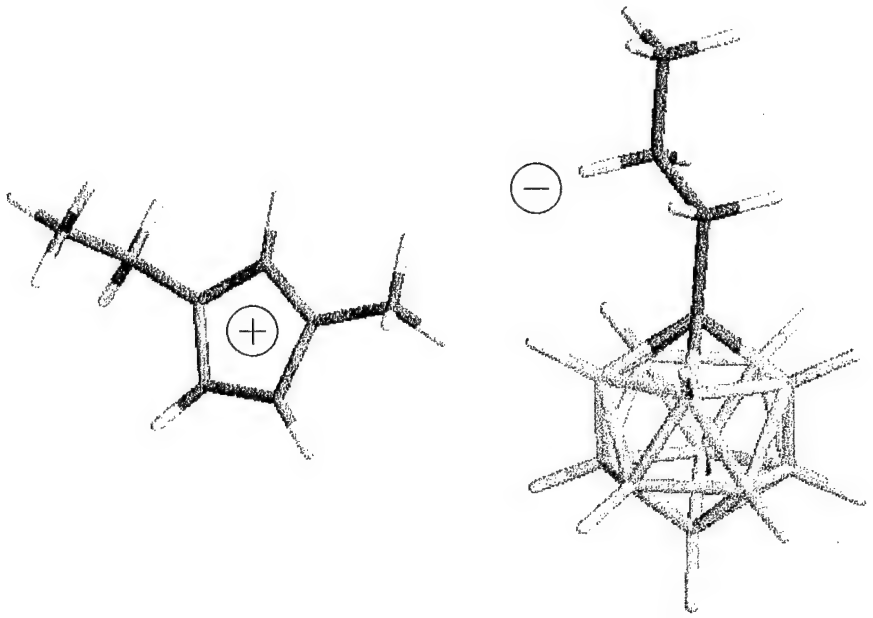
Red values in () are for corresponding CF_3SO_3- salt

Viscosity and conductivity increase with increasing chain length but intramolecular hydrogen bonding can be important. Size and "charge" of anion also significant.

Bonhote, P. ; Diaz, A. ; Papageorgiou, N. ; Kalyanasundaram, K. ; Gratzel, M. Inorg. Chem. **1996**, *35*, 1168.

Ionic Liquids

The end extreme of non-coordinating anions has been achieved through the use of carborane anion in the formation of ionic liquids. Essentially no hydrogen bonding.

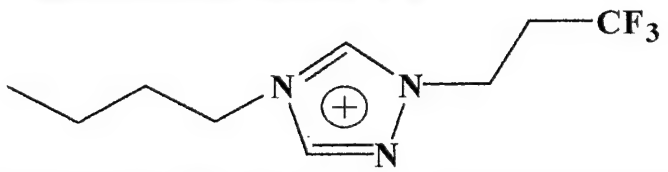


Ionic liquid	m.p. °C
[EMIM][$HCB_{11}H_{11}$]	122
[EMIM][1-CH_3-$CB_{11}H_{11}$]	59
[EMIM][1-CH_2CH_3-$CB_{11}H_{11}$]	64
[EMIM][1-$CH_2CH_2CH_3$-$CB_{11}H_{11}$]	45
[EMIM][1-$CH_2CH_2CH_2CH_3$-$CB_{11}H_{11}$]	49

1-ethyl-3-methyl-imidazolium icosahedral 1-propyl-1-carborane [EMIM][1-prop-$CB_{11}H_{11}$]

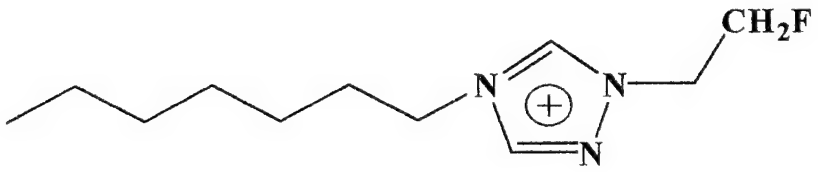
Larsen, A. S. ; Holbrey, J. D.; Tham, F. S.; Reed, C. A. J. Amer. Chem. Soc. **2000**, *122*, 7264.

Ionic Liquids



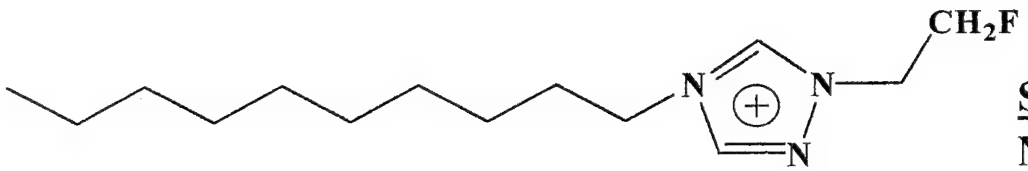
1-(3',3',3'-trifluoro-n-propyl)-3-n-butyl-1,2,4-triazolium

Salt	m.p.(°C)	DSC onset (°C)
NTf_2^-	-67	395
TfO^-	33	379



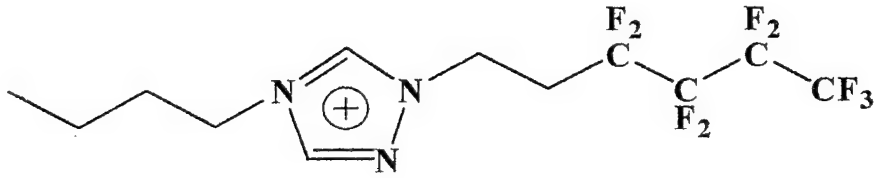
1-(2'-fluoroethyl)-3-n-heptyl-1,2,4-triazolium

Salt	m.p.(°C)	DSC onset (°C)
NTf_2^-	-70	359
BF_4^-	52	336



1-(2'-fluoroethyl)-3-n-decyl-1,2,4-triazolium

Salt	m.p.(°C)	DSC onset (°C)
NTf_2^-	-62	426
TfO^-	46	362



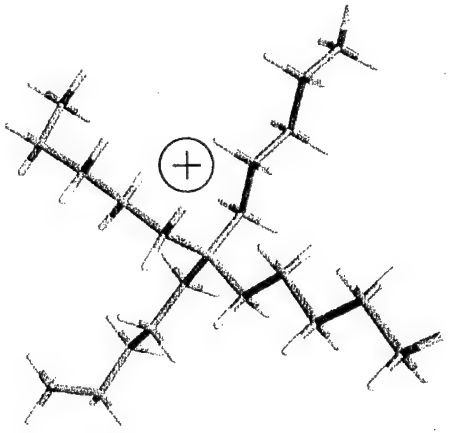
1-(1H,1H,2H,2H-perfluoro-n-hexyl)-3-n-butyl-1,2,4-triazolium

Salt	m.p.(°C)	DSC onset (°C)
NTf_2^-	69	394
TfO^-	173	391
PF_6^-	296	357

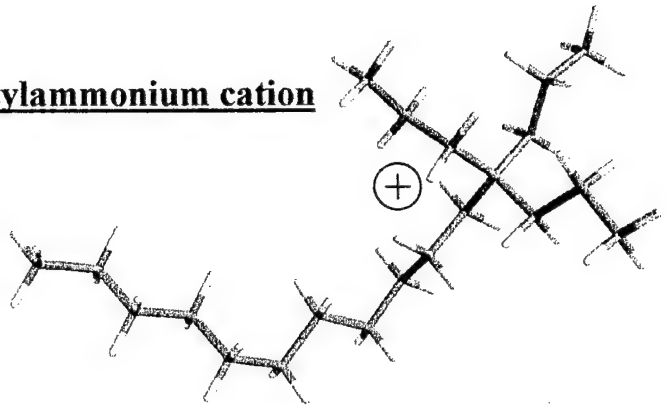
Mirzaei, Y. R. ; Twamley, B. ; Shreeve, J. M. J. Org. Chem. **2002**, *67*, 9340.

Ionic Liquids

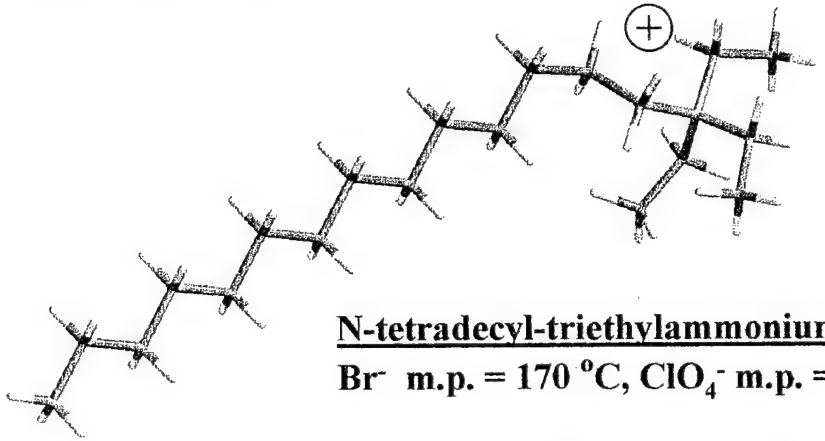
Substituted ammonium salts $R_4N^+X^-$ Variations in melting point based on cation structure.



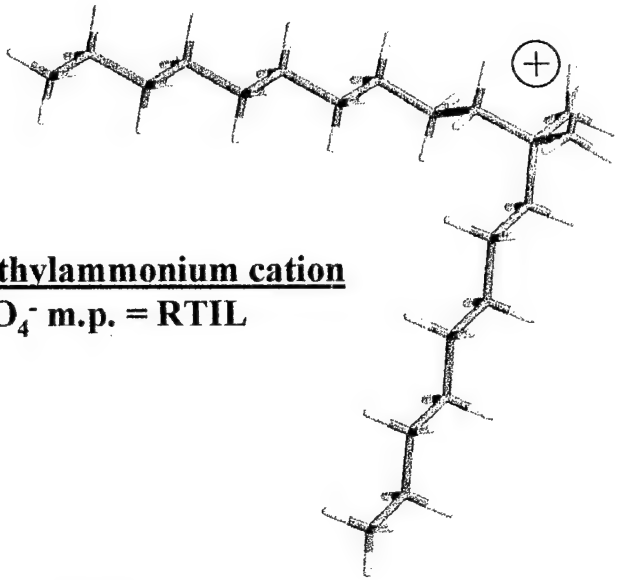
Tris-(n-propyl)-undecylammonium cation
Br^- m.p. = 67 °C
ClO_4^- m.p. = 65 °C



Tetra-n-pentylammonium cation
Br^- m.p. = 101 °C
ClO_4^- m.p. = 118 °C



N-tetradecyl-triethylammonium cation
Br^- m.p. = 170 °C, ClO_4^- m.p. = 152 °C



N-decyl-n-octyl-dimethylammonium cation
Br^- m.p. = RTIL, ClO_4^- m.p. = RTIL

Gordon, J. E. ; SubbaRao, G. N. J. Amer. Chem. Soc. **1978**, *100*, 7445.

Ionic Liquids

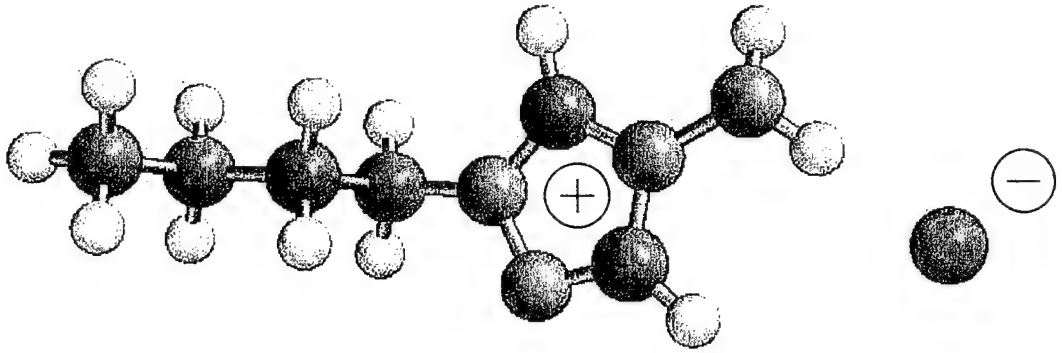
Substituted ammonium salts $[R_4N^+][X^-]$Recently work has been done by using more desirable anions.

Substituted Ammonium Salt	M.P. (° C)	Density (g/cm^3)	Viscosity (cp)	Λ (Ω^{-1} cm^2/mole)
$[(n\text{-}C_6H_{13})(CH_3)_3N^+][N(SO_2CF_3)_2^-]$	-74 (g)	1.33	153	1.4
$[(n\text{-}C_7H_{15})(CH_3)_3N^+][N(SO_2CF_3)_2^-]$	-73 (g)	1.28	153	1.4
$[(n\text{-}C_8H_{17})(CH_3)_3N^+][N(SO_2CF_3)_2^-]$	-73(g)	1.27	181	1.3
$[(n\text{-}C_6H_{13})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2^-]$	20	1.27	167	2.5
$[(n\text{-}C_7H_{15})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2^-]$	-79	1.26	75	1.9
$[(n\text{-}C_8H_{17})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2^-]$	-74	1.25	202	1.3
$[(n\text{-}C_6H_{13})(n\text{-}C_4H_9)_3N^+][N(SO_2CF_3)_2^-]$	26	1.15	595	0.8
$[(n\text{-}C_7H_{15})(n\text{-}C_4H_9)_3N^+][N(SO_2CF_3)_2^-]$	-67	1.17	606	0.8
$[(n\text{-}C_8H_{17})(n\text{-}C_4H_9)_3N^+][N(SO_2CF_3)_2^-]$	-63	1.12	574	0.7
$[(n\text{-}C_7H_{15})(Et)_3(ipr)_2N^+][N(SO_2CF_3)_2^-]$	-82	1.27	362	1.2
$[(n\text{-}C_8H_{17})(n\text{-}C_4H_9)_3N^+][OSO_2CF_3^-]$	-57	1.02	2030	0.07

-most have very low glass points
-densities decrease as expected
-viscosity increases dramatically with increasing alkyl length
-conductivity decreases with cation size (mobility issue)

Sun, J. ; Forsyth, M. ; MacFarlane, D. R. J. Phys. Chem. B **1998**, *102*, 8858.

Ionic Liquids

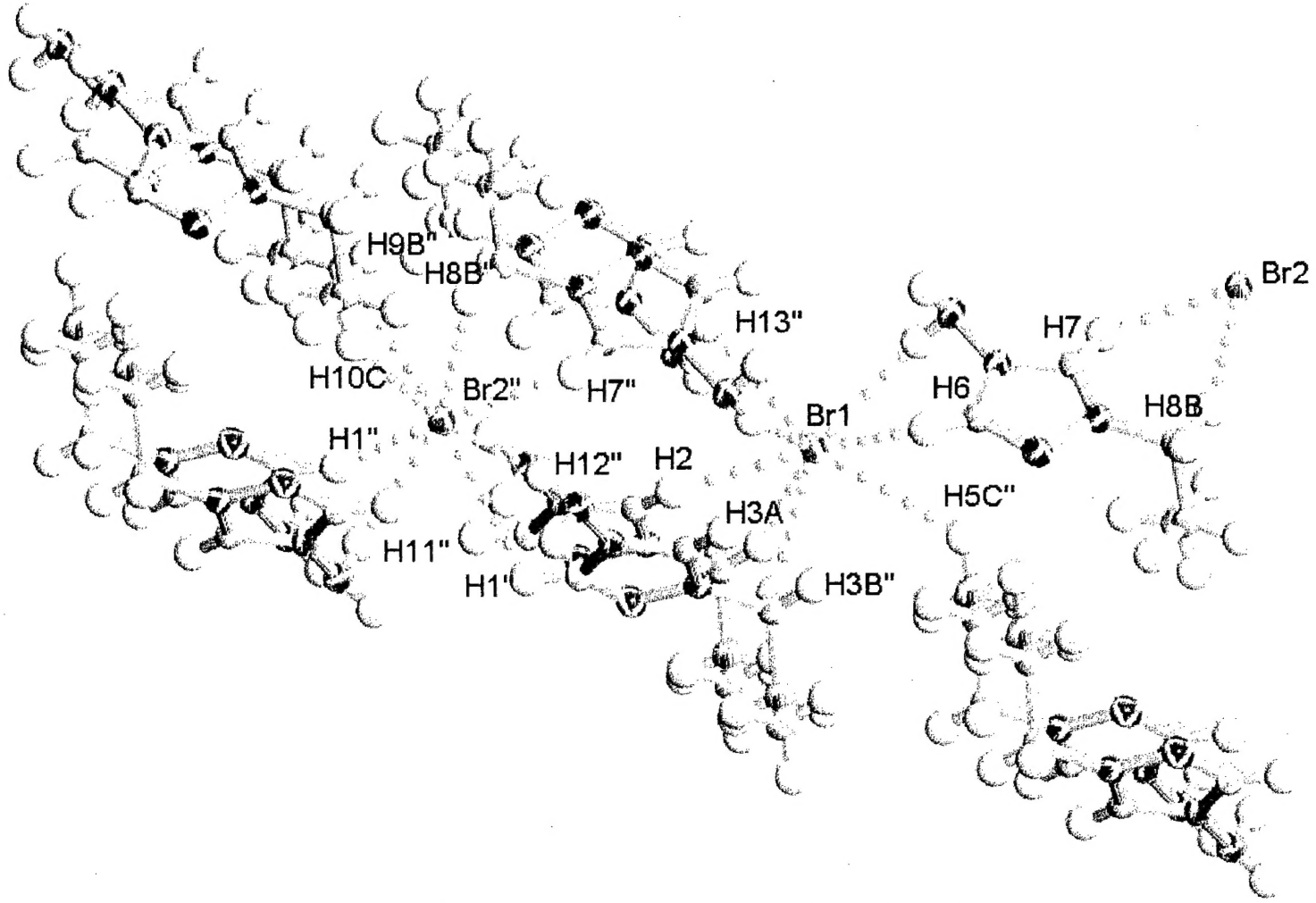


1-n-butyl-4-amino-1,2,4-triazolium bromide

1-substituted 4AT salts	m.p. (°C)	dec. onset (°C)	density (g/cm^3)
1-ethyl	63°	110	1.69
1-n-propyl	60°	120	1.56
1-isopropyl	90°	110	1.60
1-butyl	48°	130	1.46
1-n-pentyl	54°	130	1.37
1-n-hexyl	76°	120	1.34
1-n-heptyl	94°	120	1.30
1-n-octyl	80°	135	1.27
1-n-nonyl	81°	140	1.26
1-n-decyl	90°	135	1.23

[#]Drake, G. W.; Hawkins, T. W.; Tollison, K.; Hall, L.; Vij, A. **2003** manuscript in progress.

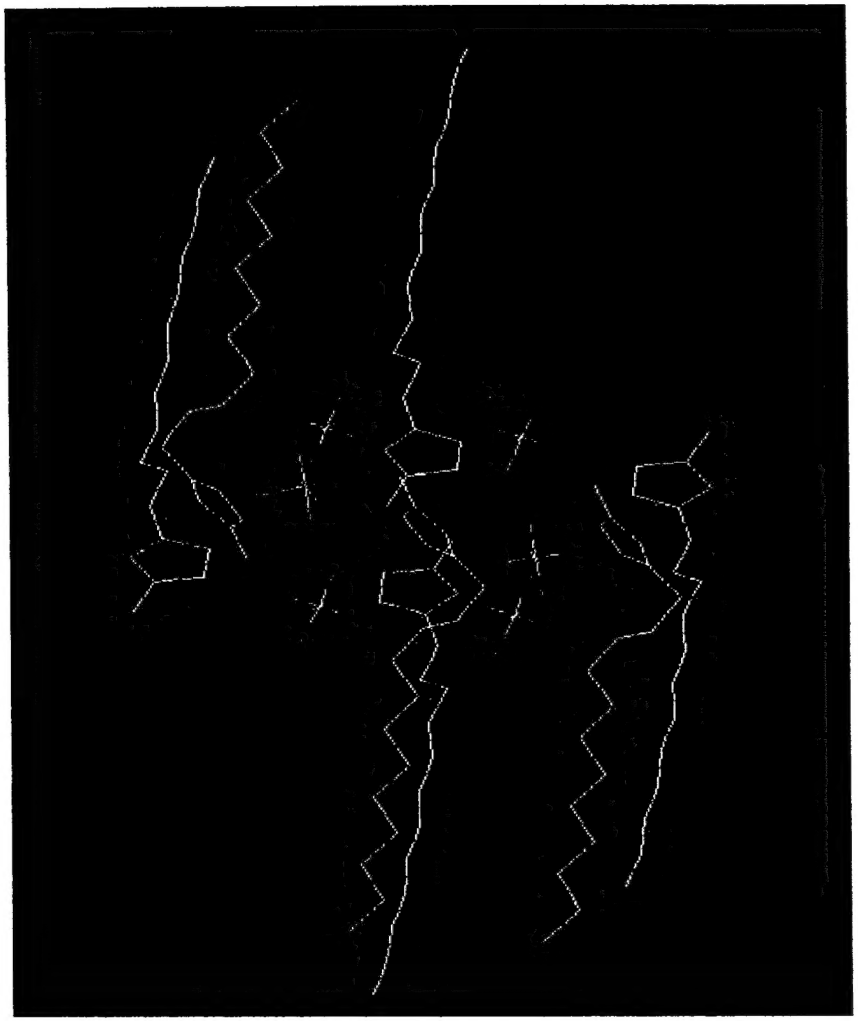
Ionic Liquids



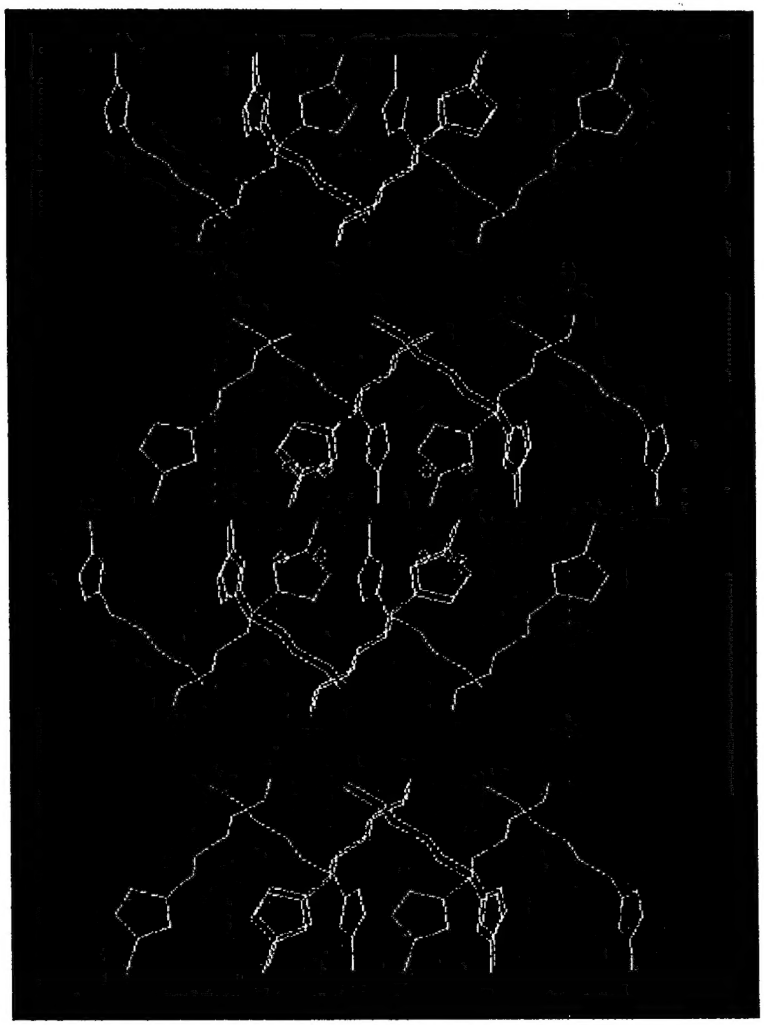
Extensive hydrogen bonding in 1-n-propyl-4-amino-1,2,4-triazolium bromide

[#]Drake, G. W.; Hawkins, T. W.; Tollison, K.; Hall, L.; Vij, A. **2003** manuscript in progress.

Ionic Liquids



1-dodecyl-3-methylimidazolium hexafluorophosphate*



1-hexyl-4-amino-1,2,4-triazolium bromide#

*Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. J. Mater. Chem. **1998**, *8*, 2627.

#Drake, G. W.; Hawkins, T. W.; Tollison, K.; Hall, L.; Vij, A. **2003** manuscript in progress.

Ionic Liquids

Summary and Conclusions

- Overall cation symmetry or lack thereof dramatically affects the physical properties of ionic liquids.

- Inter- as well as intra- molecular interactions especially hydrogen bonding are very important.

- Conductivity and viscosity are indirectly related, and both are significantly affected by the size and charge distribution of the cation and/or anion.

- New classes of ionic liquids are appearing and the field has tremendous promise for new and exciting breakthroughs.

Ionic Liquids

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